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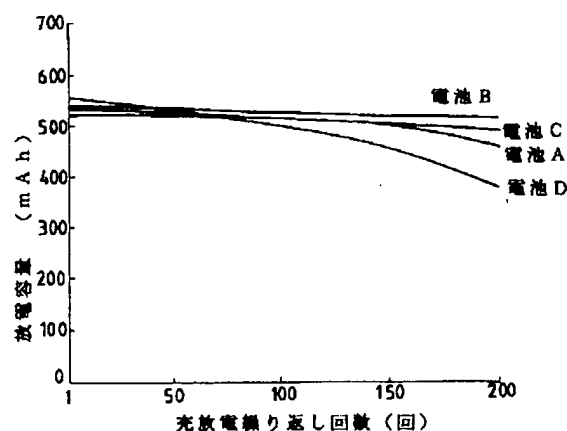
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(54) 【発明の名称】 非水電解液二次電池

(57) 【要約】

【目的】 高容量で、充放電の繰返しに伴う容量低下、および電池の保存中における劣化の少ない、特性の優れた非水電解液二次電池を提供する。

【構成】 少なくとも正極と、負極と、エステル類を含む非水電解液とからなる非水電解液二次電池において、前記正極の活物質としてニッケル酸リチウム  $\text{Li}_x\text{NiO}_2$  ( $0 < x \leq 1$ ) の表面を、コバルト酸リチウム  $\text{Li}_x\text{CoO}_2$  ( $0 < x \leq 1$ ) および、マンガン酸リチウム  $\text{Li}_x\text{MnO}_2$  ( $0 < x \leq 1$ ) のうちの少なくとも1種で被覆したものをを用いるようにした。



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# PATENT ABSTRACTS OF JAPAN

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## (54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:

PURPOSE: To provide a nonaqueous electrolyte secondary battery with high capacity, less capacity drop in accordance with charge/discharge cycles, and less deterioration in performance during storage.

CONSTITUTION: In a nonaqueous electrolyte secondary battery comprising at least a positive electrode, a negative electrode, and a nonaqueous electrolyte containing esters, as an active material of the positive electrode, lithium nicklate,  $\text{Li}_x\text{NiO}_2$  ( $0 < x \leq 1$ ) whose surface is covered with at least one of lithium cobalate,  $\text{Li}_x\text{CoO}_2$  ( $0 < x \leq 1$ ) and lithium manganate,  $\text{Li}_x\text{MnO}_2$  ( $0 < x \leq 1$ ) is used.

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## CLAIMS

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[Claim(s)]

[Claim 1] It is the nonaqueous electrolyte rechargeable battery with which it is the nonaqueous electrolyte rechargeable battery which consists of a positive electrode, a negative electrode, and nonaqueous electrolyte containing ester at least, and the active material of said positive electrode covers the front face of the nickel acid lithium  $\text{LiX NiO}_2$  ( $0 < x \leq 1$ ) with at least one sort in the cobalt acid lithium  $\text{Li}_x \text{CoO}_2$  ( $0 < x \leq 1$ ) and the manganic acid lithium  $\text{Li}_x \text{MnO}_2$  ( $0 < x \leq 1$ ).

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] Especially this invention relates to amelioration of the positive active material about a nonaqueous electrolyte rechargeable battery.

[0002]

[Description of the Prior Art] In recent years, the request to the long lasting rechargeable battery which portable-izing of electronic equipment and cordless-ization are progressing quickly, and is small and lightweight as these power sources for a drive, has a high energy consistency, and was excellent in the charge-and-discharge cycle property is high. A nonaqueous electrolyte rechargeable battery, especially a lithium secondary battery have great expectation at such a point as a cell which especially has a high voltage and a high energy consistency.

[0003] Research and development of an ingredient are briskly made in recent years for the purpose of development of the positive active material for lithium secondary batteries which fills an above-mentioned request. For example, in nickel compound relation, there is a proposal (U.S. Pat. No. 4302518 specification) of  $\text{Li}_y \text{nickel}_{2-y} \text{O}_2$  (JP,2-40861,A),  $\text{Li}_{1-x} \text{NiO}_2$ , etc., further many development examples are reported by the relation of other transition-metals compounds, and there are some which are put in practical use in part.

[0004] In those compounds, the nickel acid lithium  $\text{Li}_x \text{NiO}_2$  (it is described as  $\text{LiNiO}_2$  henceforth ( $0 < x \leq 1$ )) has a large charge-and-discharge capacity per unit weight, and has the possibility as positive active material of the nonaqueous electrolyte rechargeable battery of high capacity.

[0005] Moreover, about the electrolytic solution, the thing containing ester is applied over the lithium cell at large.

[0006]

[Problem(s) to be Solved by the Invention] However,  $\text{LiNiO}_2$  The capacity fall accompanying the repeat of charge and discharge with the cell using the nonaqueous electrolyte which considers as positive active material and contains ester, And degradation under preservation of a cell is, other compounds  $\text{Li}_x \text{CoO}_2$  (henceforth ( $0 < x \leq 1$ )), for example, cobalt acid lithium.  $\text{LiCoO}_2$  \*\* -- describing -- compared with the

cell which used the manganic acid lithium  $\text{Li}_x\text{MnO}_2$  (it is described as  $\text{LiMnO}_2$  henceforth ( $0 < x \leq 1$ )) as positive active material, it turned out that it is large.

[0007] According to [ the reaction with ester and positive active material is reported by some systems for example, ] Thomas and others (J. Electrochem.Soc., 132 (1985) 1521), it is propylene carbonate and  $\text{LiCoO}_2$ . The polymer film which is a system and makes propylene carbonate the origin on the front face of  $\text{LiCoO}_2$  is generated, and migration of the lithium ion accompanying a charge-and-discharge reaction is checked. Especially Co serves as tetravalence, and when it is left in the state of the charge which gains in oxidizing power, the reaction of positive active material and the electrolytic solution becomes remarkable. the analysis technique as the above-mentioned Thomas's and others report in which this invention persons are the same -- using --  $\text{LiNiO}_2$ ,  $\text{LiCoO}_2$ , and  $\text{LiMnO}_2$  \*\*\*\*\* -- the examined result --  $\text{LiNiO}_2$   $\text{LiCoO}_2$  and  $\text{LiMnO}_2$  The reactivity of various ester was still larger. Therefore, degradation under the capacity fall accompanying the repeat of charge and discharge in this and preservation of a cell is considered to be the cause of a large thing.

[0008]

[Means for Solving the Problem] This invention is  $\text{LiNiO}_2$  which it carries out in view of the aforementioned trouble, and is called high capacity in the purpose. Without spoiling the features, a reaction with nonaqueous electrolyte tends to be controlled and degradation under the capacity fall accompanying the repeat of charge and discharge and preservation of a cell tends to be lessened.

[0009] this invention persons are  $\text{LiNiO}_2$  as a result of repeating examination wholeheartedly. They are  $\text{LiCoO}_2$  and  $\text{LiMnO}_2$  about a front face. When covered with at least one kind, knowledge that said purpose can be attained was found out.

[0010] This invention about a nonaqueous electrolyte rechargeable battery can be accomplished based on said knowledge. At least A positive electrode, It is the nonaqueous electrolyte rechargeable battery which consists of a negative electrode and nonaqueous electrolyte containing ester. The front face of the nickel acid lithium  $\text{Li}_x\text{NiO}_2$  ( $0 < x \leq 1$ ) which is the active material of said positive electrode It is characterized by covering with at least one sort in the cobalt acid lithium  $\text{Li}_x\text{CoO}_2$  and ( $0 < x \leq 1$ ) the manganic acid lithium  $\text{Li}_x\text{MnO}_2$  ( $0 < x \leq 1$ ).

[0011] Here, as an example of representation of said ester contained in nonaqueous electrolyte, diethyl carbonate, ethylene carbonate, propylene carbonate, methyl propionate, gamma-butyrolactone, etc. can be mentioned. However,  $\text{LiNiO}_2$  in the aforementioned cell Since a reaction is a problem common to ester, it is not necessarily limited to these ester.

[0012]

[Function]  $\text{LiNiO}_2$  in this invention The depressant action of a reaction with nonaqueous electrolyte is  $\text{LiNiO}_2$ . A front face is reactant small  $\text{LiCoO}_2$  relatively to ester.  $\text{LiMnO}_2$  By being covered, it is thought that reactions, such as oxidation which is the surface reaction which occurs between ester and an active material, decomposition, and a polymerization, are controlled. furthermore, migration of the lithium ion accompanying a charge-and-discharge reaction --  $\text{LiCoO}_2$  of a surface layer  $\text{LiMnO}_2$  smooth -- being spread --  $\text{LiNiO}_2$  of the interior up to -- reaching -- charge-and-discharge capacity ---like --  $\text{LiNiO}_2$  It is thought that it is dominant and the high capacity which is the features is obtained. The reaction of ester is  $\text{LiCoO}_2$ .  $\text{LiMnO}_2$  It is  $\text{LiNiO}_2$  with the metals

(platinum, gold, etc.) which a lithium ion does not diffuse although it is still fewer, and carbon. When a front face was covered, charge-and-discharge capacity fell remarkably. the matter covered from this --  $\text{LiCoO}_2$   $\text{LiMnO}_2$  not only -- a lithium ion -- being spread -- ester -- receiving --  $\text{LiNiO}_2$  if reactivity is relatively small --  $\text{LiCoO}_2$   $\text{LiMnO}_2$

Although it is expected that the same effectiveness is acquired, the further examination for looking for such matter is needed.

[0013]

[Example] Hereafter, this invention is explained in accordance with a concrete example with a drawing.

[0014] First, the manufacture approach common to [ positive active material ] an example is shown.  $\text{LiNiO}_2$  obtained by the well-known method of mixing nickel hydroxide powder and lithium-hydroxide powder, and heating in a 700-degree C oxygen ambient atmosphere Powder By making it distribute, stirring in the water-soluble salt containing the transition metals of the compound which covers this, for example, a cobalt nitrate,/, or the water solution of manganese nitrate, and adding the water solution of alkali salt, for example, a lithium hydroxide, to this suspension Said  $\text{LiNiO}_2$  used as a nucleus The compound which contains the transition metals of the compound to cover on the surface of powder can be deposited. The precipitate obtained by stopping stirring is rinsed, it dries, and the powder of a midcourse phase is obtained.

[0015] In order to obtain a thing similar to the powder of this midcourse phase, there are other approaches. For example,  $\text{LiNiO}_2$  The method of targeting cobalt salt and/, or manganese salt into a base ingredient, and performing sputtering, and  $\text{LiNiO}_2$  Although the approach of covering cobalt salt and/, or manganese salt powder mechanochemical etc. is in powder, the approach by the deposit out of the above-mentioned solution is desirable from the viewpoint of the difficulty of manufacture, and the imperfection of covering.

[0016] It responds to the amount of the compound which deposited the powder of a midcourse phase, and is  $\text{LiCoO}_2$ . And/or  $\text{LiMnO}_2$  It heats in air with the lithium-hydroxide powder equivalent to obtaining. 2 - 3 hours is sufficient as the time amount at this time, and if it carries out for a long time, Co of a surface layer and/or Mn, and internal nickel will carry out counter diffusion, and the solid solution will be formed.

[0017] The condition of covering of the obtained active material was observed by X-ray micro analysis (XMA). An epoxy resin is made to mix and harden an active material, and if the field of the arbitration is ground, the cross section of an active material can be exposed. The mimetic diagram of the typical result obtained by drawing 1 by field analysis of XMA was shown.  $\text{LiNiO}_2$  used as a nucleus It is  $\text{LiCoO}_2$  to a front face. And/or  $\text{LiMnO}_2$  Signs that it is generating are shown. As for the inside A of drawing, the part in which nickel exists, and B show the part in which Co and/, or Mn exists.

[0018] Next, the creation approach of the cylindrical shape cell for a trial and the outline of a configuration in an example are shown below.

[0019] a positive electrode -- a mixture -- the paste was added as a solvent until it had suitable viscosity to apply a N-methyl-2-pyrrolidone to what mixed the positive active material, acetylene black, and polyvinylidene fluoride which were obtained by the above-mentioned approach by the weight ratio of 100:4:5. this positive electrode -- a mixture -- the paste was applied to both sides of aluminium foil, desiccation and rolling processing were carried out, and the positive-electrode plate was prepared. On the other hand, it

mixed the carbon material and fluororesin system binding material which calcinated corks and were obtained by the weight ratio of 100:10, respectively, kneaded this in the carboxymethyl-cellulose water solution, considered it as the paste, the negative-electrode plate was applied to both sides of copper foil, carried out desiccation and rolling processing and was prepared. Although various combination examined the electrolytic solution, since the result was the same in any case, in order to avoid \*\*\*\*, it describes for convenience the case of the electrolytic solution which dissolved and prepared lithium perchlorate at a rate of 1 mol / 1 as a supporting electrolyte to volume mixed solvents, such as propylene carbonate and ethylene carbonate, in a concrete example.

[0020] The lead was attached to the two poles of a band-like forward and negative electrode, and the whole was spirally rolled on both sides of the separator made from polypropylene. After containing this in the cell case made from stainless steel, the electrolytic solution of the specified quantity was poured in, and it equipped with other component parts, and the cell was constituted.

[0021] In this way, drawing of longitudinal section of the created cylindrical shape cell was shown in drawing 2. One in drawing shows the cell case which held the group of electrode 2, the positive-electrode lead 4 is connected to the obturation plate 3 which seals this cell case 1, and the negative-electrode lead 5 is connected to the pars basilaris ossis occipitalis of the cell case 1. 6 has the function to insulate the obturation plate 3 which is a positive-electrode terminal, and the cell case 1 where a negative-electrode terminal is made while it shows packing and maintains airtightness. The insulating ring of 7 has prevented forward and the negative-electrode plate of a group of electrode 2 contacting and connecting with the cell case 1 and the obturation plate 3 too hastily inside a cell.

[0022] (Example 1) A cobalt nitrate is used for the water-soluble salt which contains the transition metals of the compound to cover in the manufacture approach of the aforementioned positive active material, and it is  $\text{LiNiO}_2$ . It is  $\text{LiCoO}_2$  to a front face. The covered positive active material was compounded. The creation approach of the cylindrical shape cell for a trial and the configuration are the same as the aforementioned approach. Let this cell be this invention cell A.

[0023] (Example 2) Manganese nitrate is used for the water-soluble salt which contains the transition metals of the compound to cover in the manufacture approach of the aforementioned positive active material, and it is  $\text{LiNiO}_2$ . It is  $\text{LiMnO}_2$  to a front face. The covered positive active material was compounded. The creation approach of the cylindrical shape cell for a trial and the configuration are the same as the aforementioned approach. Let this cell be this invention cell B.

[0024] (Example 3) An equivalent cobalt nitrate and manganese nitrate are used for the water-soluble salt which contains the transition metals of the compound to cover in the manufacture approach of the aforementioned positive active material, and it is  $\text{LiNiO}_2$ . It is  $\text{LiCoO}_2$  to a front face. And  $\text{LiMnO}_2$  The covered positive active material was compounded. The creation approach of the cylindrical shape cell for a trial and the configuration are the same as the aforementioned approach. Let this cell be this invention cell C.

[0025] (Example 1 of a comparison)  $\text{LiNiO}_2$  which nothing has covered on the front face as positive active material It used and also is the same as said example. Let this cell be the comparison cell D.

[0026] (Experiment 1) Using these cell A-D, the charge and discharge to 200 times were repeated, and the degree of a fall of the discharge capacity was compared. The test condition at this time is 140mA constant current, and carries out the charge and discharge of each cell put on the 20-degree C ambient atmosphere in [ electrical-potential-difference ] 3.0V-4.1V.

[0027] This result is shown in drawing 3 . Drawing 3 shows that there are few degrees of a fall although discharge capacity is slightly smaller than the comparison cell D in early stages of the repeat of charge and discharge, and, as for this invention cells A, B, and C, discharge capacity becomes large from the comparison cell D after about 30 - 70 times of repeats.

[0028] (Experiment 2) Cell A-D put on the 20-degree C ambient atmosphere was left for three weeks in the 60-degree C ambient atmosphere, after charging to 4.1V by 140mA constant current. The cell after neglect was returned to the 20-degree C ambient atmosphere, and the discharge capacity after charging to 4.1V by 140mA constant current again was measured. This evaluated the degree of degradation by neglect.

[0029] This result is shown in Table 1.

[0030]

[Table 1]

	放電容量 (mAh)
本発明電池 A	4 9 7
本発明電池 B	5 1 1
本発明電池 C	5 0 2
比較電池 D	4 1 9

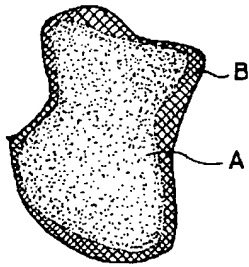
[0031] From Table 1, this invention cells A, B, and C are understood that discharge capacity is large and there is less degradation by neglect than the comparison cell D.

[0032]

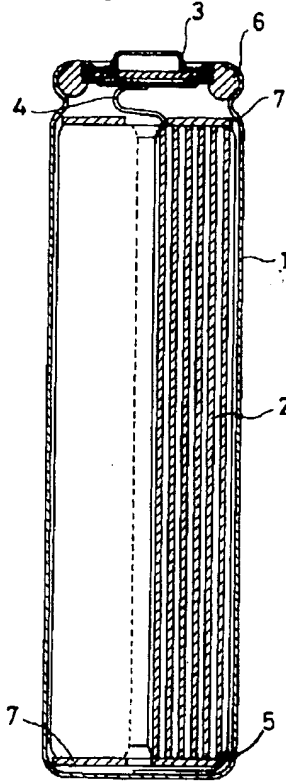
[Effect of the Invention] In the nonaqueous electrolyte rechargeable battery which consists of a positive electrode, a negative electrode, and nonaqueous electrolyte containing ester at least according to this invention so that clearly from the above explanation The front face of the nickel acid lithium  $\text{LiX NiO}_2$  ( $0 < x \leq 1$ ) which is positive active material By covering with at least one sort in the cobalt acid lithium  $\text{LiX CoO}_2$  and ( $0 < x \leq 1$ ) the manganic acid lithium  $\text{LiX MnO}_2$  ( $0 < x \leq 1$ )  $\text{LiNiO}_2$  called high capacity Without spoiling the features, a reaction with nonaqueous electrolyte can be controlled and a nonaqueous electrolyte rechargeable battery with little degradation under the capacity fall accompanying the repeat of charge and discharge and preservation of a cell can be offered.

Drawing 1

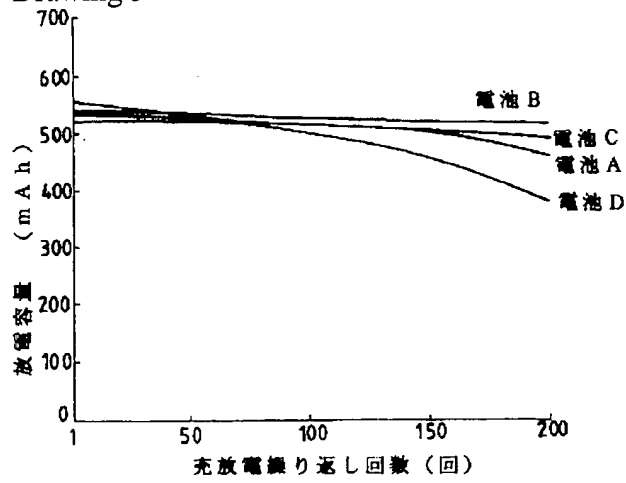




Drawing 2



Drawing 3



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